

AD-A062 661

CALIFORNIA UNIV BERKELEY DEPT OF CHEMICAL ENGINEERING F/G 20/4
A KINETIC NETWORK MODEL FOR NONLINEAR VISCOELASTIC FLOW PROPERT--ETC(U)
NOV 78 D SOONG, M SHEN N00014-75-C-0955
TR-21 NL

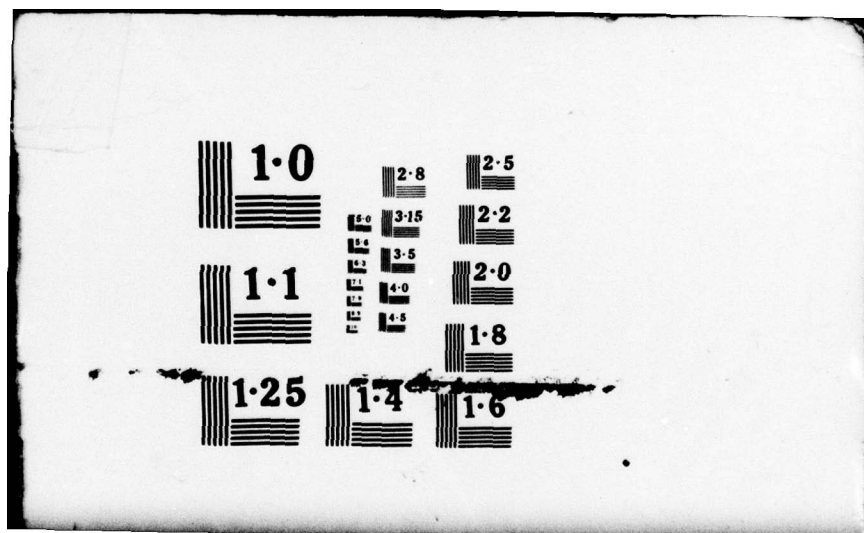
UNCLASSIFIED

1 OF 1
ADA
062661



END
DATE
FILMED

3 -79
DDC



12 LEVEL II
NW

OFFICE OF NAVAL RESEARCH

Contract ¹⁵ ~~NO~~ 014-75-C-0955

Task No. NR 356-526

14 TR-21

9 TECHNICAL REPORT NO. 21

6 A Kinetic Network Model

for Nonlinear Viscoelastic Flow Properties
of Entangled Monodisperse Polymers.

by

10 David/Soong ~~and~~ Mitchel/Shen

Prepared for Publication

in

Polymer Letters

DDC
RECEIVED
DEC 29 1978
B

University of California, Berkeley
Department of Chemical Engineering
Berkeley, California

11 25 Nov ~~1978~~ 78

12 12p.

Reproduction in whole or in part is permitted for
any purpose of the United States Government

*This document has been approved for public release
and sale; its distribution is unlimited

78 12 26 029

404 601

Gu

ADA062661

DDC FILE COPY

A KINETIC NETWORK MODEL FOR NONLINEAR VISCOELASTIC FLOW
PROPERTIES OF ENTANGLED MONODISPERSE POLYMERS

High polymers in concentrated solutions or in the melt exhibit shear-rate-dependent viscosity and normal stress differences. In transient flows upon inception of steady shear, the stress growth function of the polymer overshoots through a maximum and then decays to the steady-state value asymptotically for large shear rates. However, for small shear rates, it only increases monotonically to its limiting steady-state value. Upon cessation of steady shear, the stress relaxation function decreases monotonically to zero, the rate of which is higher for larger shear rates. These rheological properties have been interpreted by the shear-induced changes in the steady-state entanglement density in the polymer (1).

Lodge explained the nonlinear viscoelastic flow properties by a "rubberlike liquid" model, which however still predicted a shear-rate-independent viscosity and primary normal stress coefficient. Many modified theories (3-6) have since been proposed to refine this model. Most of them employ empirical expressions for the memory functions to give the rate-dependent properties. In this work, we shall propose a kinetic network model which appears to predict the observed nonlinear viscoelastic flow properties of entangled polymer systems.

The basic molecular mechanism of this model attributes the rate-dependence of viscosity and normal stress difference to the decrease in entanglement density with increasing shear rate. In a flow field, entanglements are being formed and disengaged

78 12 26 029

→ constantly. The entanglement loss process is caused primarily by the imposed shear and is assumed to be proportional to the shear rate to a power a where

$$\dot{n}_l = k_l \dot{\gamma}^a n \quad (1)$$

where \dot{n}_l is the entanglement loss rate, k_l is the rate constant, $\dot{\gamma}$ is the shear rate, n is the current number of entanglements along a representative chain, and $a (<1)$ accounts for the elastic nature of the polymer. The entanglement creation process, driven by thermal diffusion, is assumed to be independent of shear rate. ↩
In other words,

$$\dot{n}_c = (k_c / \lambda^a) (n_0 - n) \quad (2)$$

where \dot{n}_c is the entanglement creation rate, k_c is the rate constant, λ is a characteristic time determined by the rate of diffusion, and is thus a function of molecular weight and temperature, a is the elasticity parameter, and n_0 is the saturation number of entanglements along a representative chain. $(n_0 - n)$ is the number of vacant sites where entanglements have been lost and can be likely regenerated.

At steady state, the creation rate equals the loss rate ($\dot{n}_c = \dot{n}_l$) and the entanglement density stays constant. Equating Eqs. 1 and 2, we have

$$P \equiv n/n_0 = \frac{1}{1 + (k_l/k_c) (\lambda \dot{\gamma})^a} \quad (3)$$

Eq. 3 describes the probability for entanglements to exist at different shear rates. The viscous drag from the entanglements is believed to be the major source of contribution to polymer viscosity (1). Therefore, to a good approximation, the reduced

Section <input checked="" type="checkbox"/>		
Division <input type="checkbox"/>		
SPECIAL <input type="checkbox"/>		
CITY CODES		
or SPECIAL		
A		

viscosity as a function of shear rate is also given by

$$\frac{\eta(\dot{\gamma})}{\eta_0} = \frac{1}{1 + (k_\ell/k_c) (\lambda \dot{\gamma})^a} \quad (4)$$

where η_0 is the zero-shear-rate viscosity of the polymeric fluid.

The normal stresses come from the elastic energy stored in the system, and are primarily sustained by pairs of entanglements, because the elastic deformation energy can be trapped in between these slowly moving points. The primary normal stress difference should thus be proportional to the square of the probability for individual entanglements to remain under the flow situation, which in turn corresponds to the probability for pairs of entanglements to exist simultaneously. In other words,

$$\tau_{11}(\dot{\gamma}) - \tau_{22}(\dot{\gamma}) = -\theta \left(\frac{\dot{\gamma}}{1 + (k_\ell/k_c) (\lambda \dot{\gamma})^a} \right)^2 \quad (5)$$

where θ is a proportionality constant which determines the value of primary normal stress difference. The reduced viscosity and primary normal stress difference as functions of shear rate calculated by Eqs. 4 and 5 for a equals to 0.85 is given in Fig. 1. The curves show qualitatively the expected trend.

Under transient flow conditions, such as inception and cessation of steady shear, the entanglement probability P becomes a function of time which also has some parametric dependence on shear rate. It can still be calculated by the following differential equation governing the relationship between the change of entanglements to the two competing rate processes, i.e.,

$$\dot{n} = \dot{n}_c - \dot{n}_l \quad (6)$$

where \dot{n} is the rate of change of entanglements. Inserting the expressions for entanglement creation and loss rates, Eq. 6 can be integrated to give for start-up experiments.

$$P(t; \dot{\gamma}_0) = P_\infty(\dot{\gamma}_0) + (1 - P_\infty(\dot{\gamma}_0)) \exp\left(\frac{-k_l \dot{\gamma}_0^a t}{1 - P_\infty(\dot{\gamma}_0)}\right) \quad (7)$$

where $P_\infty(\dot{\gamma}_0)$ is the steady-state entanglement probability; and for stress relaxation experiments.

$$P(t; \dot{\gamma}_0) = 1 - (1 - P_\infty(\dot{\gamma}_0)) \exp\left(-\frac{k_c}{\lambda^a} t\right) \quad (8)$$

where $P_\infty(\dot{\gamma})$ is again the steady-state entanglement probability, in this case, before the flow is stopped.

Polymer network possesses certain elastic characteristics. When it is suddenly deformed upon the inception of steady shear, the shear stress born by an average entanglement first increases with time rapidly and then gradually levels off towards the steady-state value. A Maxwellian model is assumed to represent this behavior, i.e.,

$$\frac{\sigma(t; \dot{\gamma}_0)}{\sigma_\infty(\dot{\gamma}_0)} = 1 - \exp(-t/\tau) \quad (9)$$

where $\sigma(t; \dot{\gamma}_0)$ and $\sigma_\infty(\dot{\gamma}_0)$ are the current average stress and the final steady-state stress carried by individual entanglements respectively, and τ is the system time constant. The macroscopic stress exerted by the fluid is given by the product of the average microstress supported by a remaining entanglement and the number of such stress-bearing entanglements. The

normalized shear stress growth functions thus calculated are presented in Fig. 2. The curves qualitatively reproduce the expected behavior. Quantitative comparison of this theory with experimental data is now being investigated, the results of which will be reported in forthcoming publications.

REFERENCES

1. W.W. Graessley, *Advances in Polymer Science*, 16 (1974)
2. A.S. Lodge, "Elastic Liquids" Academic Press, London and N.Y. (1964)
3. P.J. Carreau, *Trans. Soc. Rheol.*, 16, 99 (1972)
4. A. Kaye, *Brit. J. Appl. Phys.*, 17, 803 (1966)
5. M. Yamamoto, *J. Phys. Soc. Japan*, 11, 413 (1956); 12, 1148 (1957); 13, 1200 (1958)
6. R.I. Tanner and J.M. Simmons, *Chem. Eng. Sci.*, 22, 1803 (1967)

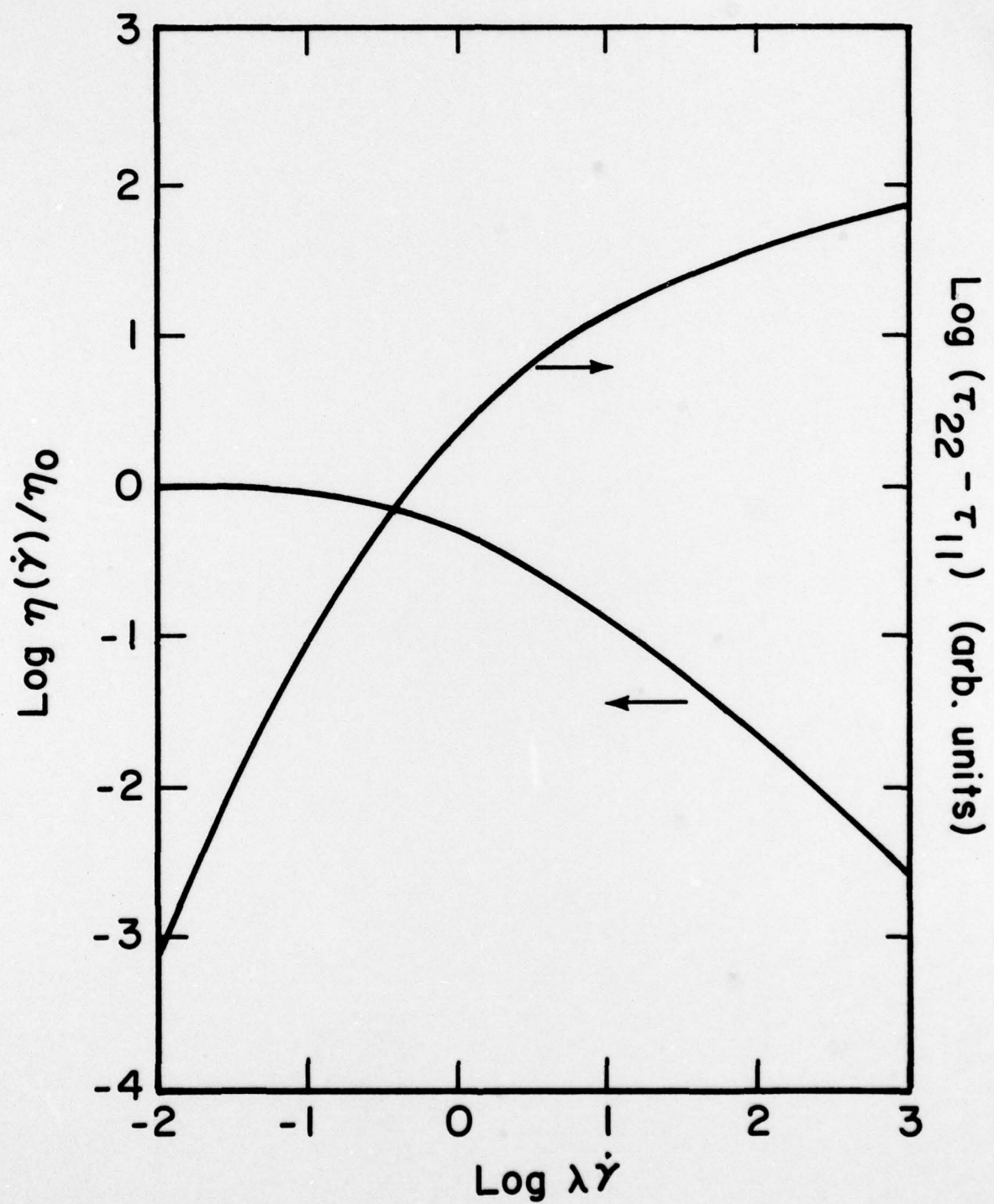
David Soong

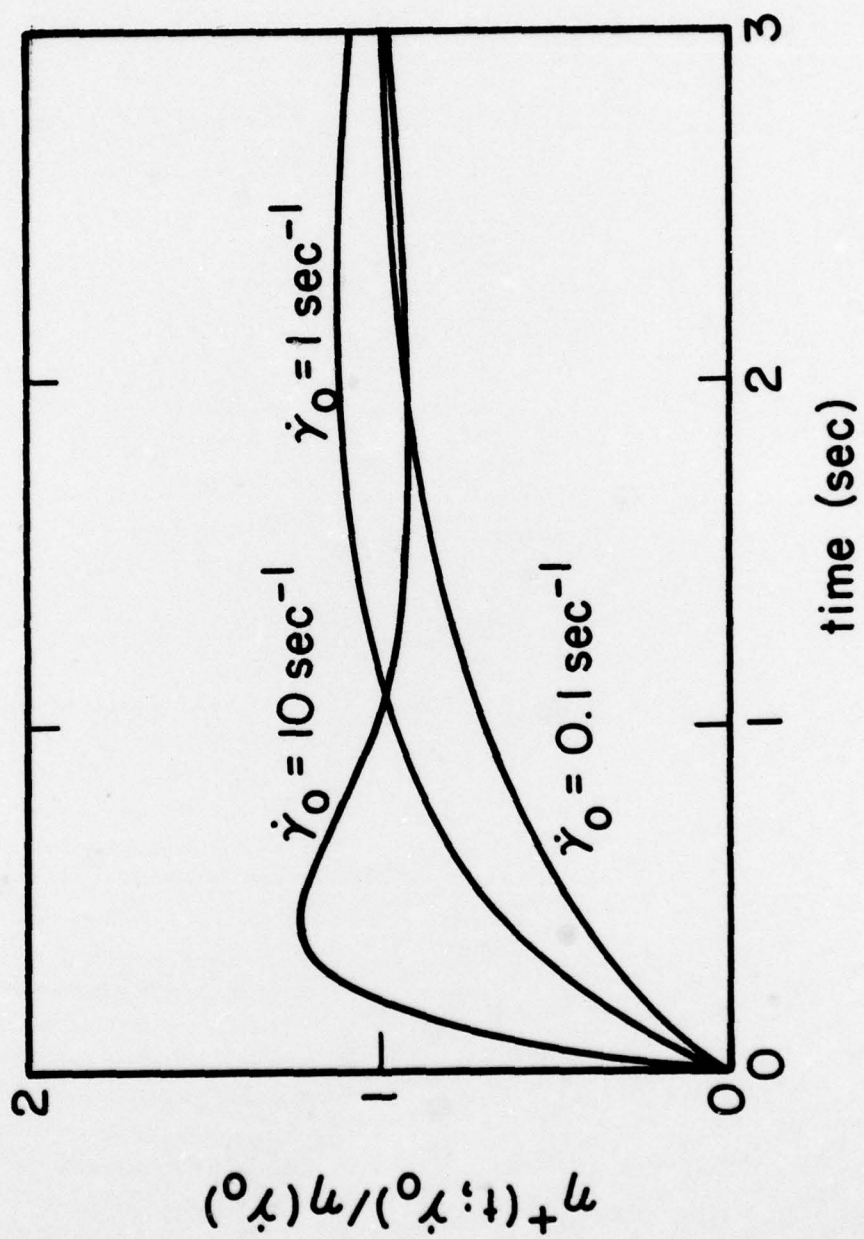
Mitchel Shen

Department of Chemical Engineering
University of California, Berkeley
Berkeley, California 94720

CAPTIONS

1. Theoretical curves of log reduced viscosity and primary normal stress difference vs log reduced shear rate, where λ is the characteristic time, and a is the elasticity parameter. (The ratio k_ℓ/k_c is taken as 1, and $a = 0.85$)
2. Normalized stress growth function for three different shear rates calculated by the theory. The parameters used are $a = 0.85$, $k_\ell = 0.3$, $k_\ell/k_c \lambda^a = 1$, $\tau = 0.5$.





TECHNICAL REPORT DISTRIBUTION LIST, GEN

	<u>No.</u> <u>Copies</u>		<u>No.</u> <u>Copies</u>
Office of Naval Research 800 North Quincy Street Arlington, Virginia 22217 Attn: Code 472	2	Defense Documentation Center Building 5, Cameron Station Alexandria, Virginia 22314	12
ONR Branch Office 536 S. Clark Street Chicago, Illinois 60605 Attn: Dr. George Sandoz	1	U.S. Army Research Office P.O. Box 1211 Research Triangle Park, N.C. 27709 Attn: CRD-AA-IP	1
ONR Branch Office 715 Broadway New York, New York 10003 Attn: Scientific Dept.	1	Naval Ocean Systems Center San Diego, California 92152 Attn: Mr. Joe McCartney	1
ONR Branch Office 1030 East Green Street Pasadena, California 91106 Attn: Dr. R. J. Marcus	1	Naval Weapons Center China Lake, California 93555 Attn: Dr. A. B. Amster Chemistry Division	1
ONR Area Office One Hallidie Plaza, Suite 601 San Francisco, California 94102 Attn: Dr. P. A. Miller	1	Naval Civil Engineering Laboratory Port Hueneme, California 93401 Attn: Dr. R. W. Drisko	1
ONR Branch Office Building 114, Section D 666 Summer Street Boston, Massachusetts 02210 Attn: Dr. L. H. Peebles	1	Professor K. E. Woehler Department of Physics & Chemistry Naval Postgraduate School Monterey, California 93940	1
Director, Naval Research Laboratory Washington, D.C. 20390 Attn: Code 6100	1	Dr. A. L. Slafkosky Scientific Advisor Commandant of the Marine Corps (Code RD-1) Washington, D.C. 20380	1
The Assistant Secretary of the Navy (R,E&S) Department of the Navy Room 4E736, Pentagon Washington, D.C. 20350	1	Office of Naval Research 800 N. Quincy Street Arlington, Virginia 22217 Attn: Dr. Richard S. Miller	1
Commander, Naval Air Systems Command Department of the Navy Washington, D.C. 20360 Attn: Code 310C (H. Rosenwasser)	1	Naval Ship Research and Development Center Annapolis, Maryland 21401 Attn: Dr. G. Bosmajian Applied Chemistry Division	1
		Naval Ocean Systems Center San Diego, California 91232 Attn: Dr. S. Yamamoto, Marine Sciences Division	1

Encl 1

TECHNICAL REPORT DISTRIBUTION LIST, 356A

	<u>No.</u> <u>Copies</u>		<u>No.</u> <u>Copies</u>
Dr. Stephen H. Carr Department of Materials Science Northwestern University Evanston, Illinois 60201	1	Picatinny Arsenal SMUPA-FR-M-D Dover, New Jersey 07801 Attn: A. M. Anzalone Building 3401	1
Dr. M. Broadhurst Bulk Properties Section National Bureau of Standards U.S. Department of Commerce Washington, D.C. 20234	2	Dr. J. K. Gillham Princeton University Department of Chemistry Princeton, New Jersey 08540	1
Dr. T. A. Litovitz Department of Physics Catholic University of America Washington, D.C. 20017	1	Douglas Aircraft Co. 3855 Lakewood Boulevard Long Beach, California 90846 Attn: Technical Library Cl 290/36-84 AUTO-Sutton	1
Dr. R. V. Subramanian Washington State University Department of Materials Science Pullman, Washington 99163	1	Dr. E. Baer Department of Macromolecular Science Case Western Reserve University Cleveland, Ohio 44106	1
Dr. M. Shan Department of Chemical Engineering University of California Berkeley, California 94720	1	Dr. K. D. Pae Department of Mechanics and Materials Science Rutgers University New Brunswick, New Jersey 08903	1
Dr. V. Stannett Department of Chemical Engineering North Carolina State University Raleigh, North Carolina 27607	1	NASA-Lewis Research Center 21000 Brookpark Road Cleveland, Ohio 44135 Attn: Dr. T. T. Serofini, MS-49-1	1
Dr. D. R. Uhlmann Department of Metallurgy and Material Science Center for Materials Science and Engineering Massachusetts Institute of Technology Cambridge, Massachusetts 02139	1	Dr. Charles H. Sherman, Code TD 121 Naval Underwater Systems Center New London, Connecticut	1
Naval Surface Weapons Center White Oak Silver Spring, Maryland 20910 Attn: Dr. J. M. Augl Dr. B. Hartman	1	Dr. William Risen Department of Chemistry Brown University Providence, Rhode Island 02192	1
Dr. G. Goodman Globe Union Incorporated 5757 North Green Bay Avenue Milwaukee, Wisconsin 53201	1	Dr. Alan Gent Department of Physics University of Akron Akron, Ohio 44304	1

TECHNICAL REPORT DISTRIBUTION LIST, 356A

	<u>No.</u> <u>Copies</u>		<u>No.</u> <u>Copies</u>
Mr. Robert W. Jones Advanced Projects Manager Hughes Aircraft Company Mail Station D 132 Culver City, California 90230	1	Dr. T. J. Reinhart, Jr., Chief Composite and Fibrous Materials Branch Nonmetallic Materials Division Department of the Air Force Air Force Materials Laboratory (AFSC) Wright-Patterson Air Force Base, Ohio	1 45433
Dr. C. Giori IIT Research Institute 10 West 35 Street Chicago, Illinois 60616	1	Dr. J. Lando Department of Macromolecular Science Case Western Reserve University Cleveland, Ohio 44106	
Dr. M. Litt Department of Macromolecular Science Case Western Reserve University Cleveland, Ohio 44106	1	Dr. J. White Chemical and Metallurgical Engineering University of Tennessee Knoxville, Tennessee 37916	1
Dr. E. S. Roe Department of Materials Science and Metallurgical Engineering University of Cincinnati Cincinnati, Ohio 45221	1	Dr. J. A. Manson Materials Research Center Lehigh University Bethlehem, Pennsylvania 18015	1
Dr. L. E. Smith U.S. Department of Commerce National Bureau of Standards Stability and Standards Washington, D.C. 20234	1	Dr. R. F. Helmreich Contract RD&E Dow Chemical Co. Midland, Michigan 48640	1
Dr. Robert E. Cohen Chemical Engineering Department Massachusetts Institute of Technology Cambridge, Massachusetts 02139	1	Dr. R. S. Porter University of Massachusetts Department of Polymer Science and Engineering Amherst, Massachusetts 01002	1
Dr. David Roylance Department of Materials Science and Engineering Massachusetts Institute of Technology Cambridge, Massachusetts 02039	1	Professor Garth Wilkes Department of Chemical Engineering Virginia Polytechnic Institute and State University Blacksburg, Virginia 24061	1
Dr. T. P. Conlon, Jr., Code 3622 Sandia Laboratories Sandia Corporation Albuquerque, New Mexico	1	Dr. Kurt Baum Fluorochem Inc. 6233 North Irwindale Avenue Azusa, California 91702	1
Dr. Martin Kaufmann, Head Materials Research Branch, Code 4542 Naval Weapons Center China Lake, California 93555	1	Professor C. S. Paik Sung Department of Materials Sciences and Engineering Massachusetts Institute of Technology Cambridge, Massachusetts 02139	1